MEASUREMENT AND MODELING OF NO_x OFFGASING FROM FEP TEFLON CHAMBERS

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A. Introduction

The College of Engineering, Center for Environmental Research and Technology (CE-CERT) at the University of California (UCR) is undertaking a new project to develop a "Next Generation" environmental chamber for evaluating chemical mechanisms under lower pollutant conditions than has previously been possible (Carter et al., 1999). A major objective of this project is to generate mechanism evaluation data under very low NO_x conditions, where the products and mechanisms for many VOC oxidations are expected to differ from those under the higher NO_x conditions characteristic of more polluted urban areas and the current environmental chamber data base.

One major obstacle that will limit the extent to which environmental chambers can generate useful mechanism evaluation data under low NO_x conditions is offgasing of NO_x from the walls of environmental chambers. Evidence for NO_x offgasing comes from the formation of O_3 in "pure air" irradiations, which cannot occur to any significant extent in the absence of NO_x, the observation of PAN formation in acetaldehyde - air irradiations, and other data (see Carter and Lurmann, 1991, and references therein.) In addition, NO_x offgasing in the form of HONO is considered to be the most likely explanation for the "unknown chamber radical source", which also significantly complicates mechanism evaluation using environmental chamber data (Carter et al, 1982, 1995a,b)

In this paper, we give a brief summary of preliminary analysis of previous and new data obtained concerning NO_x offgasing from environmental chamber surfaces. The emphasis will be on NO_x offgasing from indoor chambers constructed of FEP Teflon film, since this is currently the preferred material for constructing chamber walls because of its relative inertness and good light transmission properties. However, data from a chamber with a different type of surface will also be presented, for comparison.

B. Methods

1. Characterization of NO_x Offgasing and the Chamber Radical Source

NO_x offgasing in environmental chamber systems can be evaluated using several different methods. The most straightforward is simply measuring NO_x buildup in the dark in a chamber containing no NO_x initially. There has been limited data on this in the past because of limitations in sensitivities of NO_x analyzers. However, state-of-the-art TECO NO_x analyzers can monitor NO and "NOx" species at sub-ppb sensitivity, and research instruments can obtain data at lower concentrations.

Pure air irradiations can provide a more sensitive measurement of NO_x offgasing because the amount of O_3 formed is highly sensitive to the amount of NO_x offgasing occurring. The NO_x offgasing rate in the chamber can then be estimated by adjusting the offgasing rate so that model simulations fit the chamber data. Unfortunately, O_3 formation in pure air experiments is also sensitive to background levels of CO and reactive VOCs, which are uncertain in many cases. If the model does not have the correct amount of such VOCs (which may not all be detected), then the amount of NO_x offgasing derived by modeling will not be correct.

Modeling O_3 formation in acetaldehyde - air or CO - air irradiations is provides an equally sensitive means to assess NO_x offgasing effects in environmental chamber systems, without the confounding effects of uncertainties in the background VOC levels. O_3 formation in such experiments is equally sensitive to NO_x offgasing as it is in pure air runs, but the presence of known amounts of reactive VOCs means that uncertainties in background VOCs is not important in affecting modeling results. Thus, these data provide less ambiguous indirect determination of NO_x offgasing. Acetaldehyde - air runs have the additional advantage of forming PAN, which provides direct evidence for the presence of NO_x in the system, and additional data for model evaluation.

Because of the possibility that NO_x offgasing is related to the chamber radical source, measurements of the magnitude of the chamber radical source is also of interest. This can be measured by modeling NO_x - air irradiations with tracer compounds present to measure radical levels (Carter et al, 1982), and also by modeling n-butane - NO_x environmental chamber experiments, whose results are highly sensitive to this effect. Recently, we found that modeling n-butane results give much more consistent and reliable measurements of the chamber radical source than tracer - NO_x experiments (Carter et al, 1995b) in reactors constructed of Teflon film, so this is the preferred type of characterization experiment for this purpose.

2. Environmental Chambers Examined

Results of experiments relevant to characterizing NO_x offgasing and the chamber radical source were examined in four different environmental chamber systems, which represent two types of surfaces and different levels of "cleaning" between experiments and chamber history in terms of NO_x exposure. These are summarized on Table 1, and briefly discussed further below.

New Teflon Reactors. As indicated on the table, the chamber employed in this work represents our current best effort to minimize NO_x offgasing effects. The reactor was constructed of 2 mil FEP Teflon film that was wiped with purified water and dried before construction. This procedure was used to remove any atmospheric NO_x or nitrates that may have deposited on the walls. It is tube shaped and was constructed by heat-sealing 2 ~5' x 12' sheets together. It was placed inside a larger tube shaped FEP reactor that was flushed with purified air. The purified air was treated with Purafill to remove NO to below 0.05 and NO_x species to below ~0.2 ppb. The detection limit of our instrument is estmated to be 0.05 ppt as NO. The inner reactor was never knowingly exposed to NO_x, other than what was offgased in the offgasing experiments.

Table 1. Summary of major relevant characteristics of environmental chamber systems examined.

Chamber	Surface	Cleaning Method	RH
This Work	New FTP Teflon film. Wiped with H_2O before construction	NO_x never injected into reactor. Emptied and filled several times between experiments. Reactor located inside 2nd Teflon bag flushed with clean air to prevent NO_x permeation from outside.	Dry
TVA Chamber	Well-used FEP Teflon panels	Flushed with lights on for two days between runs. Typically exposed to no more than ~50 ppb NO_x.	~20%
CE-CERT DTC	Well-used FEP Teflon film	Flushed between runs. Typically exposed to 200-500 ppb NO_x.	Dry
SAPRC EC	Teflon-coated aluminum cylinder with quartz end windows.	Evacuated between experiments.	~50%

Ozone and CO were monitored using conventional laboratory instruments used for this purpose. NO and "NO_x" species were monitored using a TECO model 42CY NO -NO_x analyzer. Note that the "NO_x" measurement (also referred to as "NO_c" for NO - converter) works by converting NO_x species to NO using a heated Molybdenum converter, which efficiently converts HONO and HNO_3 as well as NO_2. For these experiments, the converter was located next to the chamber with minimum sampling lines, to minimize loss of HNO_3 on sampling lines coming to the converter. Because it was found that the converter had a "memory" effect when measuring low levels of NO_x, the NO_x analyzer was kept on pure air when it was not sampling the reactor. This was also used to establish the "zero" level, which is important when monitoring species at such low levels. To minimize loss of volume to permit multi-day experiments, sampling was done only intermittently. When monitoring NO in the presence of O_3 in the irradiations, a correction was made for loss of NO with O_3 in the dark in the sample lines.

The experiments carried out in this reactor consisted of pure air irradiations and CO - air irradiations. In each case the irradiation followed a period where the pure air or CO - air mixture sat in the dark to permit offgasing to occur. The reactor was emptied and filled at least three times between each experiment, which was sufficient to reduce the NO_x, O_3, and CO from the previous run to be diluted to below detectable levels.

TVA Chamber. The TVA chamber is described by Simonaitis and co-workers (Simonaitis and Bailey, 1995; Bailey et. al, 1996). As with this project, the objective of the TVA chamber project was to conduct mechanism evaluation chamber data at very low VOC and NO_x levels. Thus, this chamber represents the current state of the art in this regard, though it is unfortunately no longer operational. It is a relatively large indoor chamber with walls made from "Teflon panels". When it was running, it was used primarily for experiments with ~25-100 ppb NO_x, and long flushing periods were used between runs to clean the chamber. The above-referenced reports, which can be obtained from the EPA, can be consulted for details on the experimental procedures and data obtained.

Unfortunately, the only experiments conducted in this chamber that could be used to assess NO_x offgasing were two acetaldehyde - air runs. Several n-butane - NO_x experiments were carried out in this chamber, and a few of these runs were modeled to estimate the magnitude of the chamber radical source.

CE-CERT DTC. The CE-CERT Dividable Teflon Chamber (DTC) consists of two ~5000-liter reaction bags constructed of 2 mil FEP Teflon film. As discussed in various reports (see for example Carter et al, 1997 and other CE-CERT reports that can be downloaded from http://cert.ucr.edu/~carter/bycarter.htm), this chamber has been extensively used for assessing ozone reactivities of various VOCs, which involves conducting multiple irradiations with NO_x levels up to ~0.5 ppm. Thus, this represents a chamber with similar surfaces as the TVA chamber and the "clean" reactor used in this work, but with no special procedures for conducting low NO_x experiments. Pure air, acetaldehyde - air and n-butane - NO_x characterization runs are periodically carried out to assess NO_x offgasing and other chamber effects.

SAPRC EC. The SAPRC Evacuable Chamber (EC) consists of a ~6000-liter aluminum cylinder with the interior surface coated with FEP Teflon with quartz end windows. The chamber and procedures employed when operating it, are described by Carter et al (1995a). Experiments are carried out using various NO_x levels, and the chamber is evacuated between experiments. A limited number of acetaldehyde - air experiments were conducted in this chamber to determine NO_x offgasing rates, and there is a large data base of radical source characterization runs (Carter et al, 1995a).

3. Wall Model Employed

The physical and chemical processes responsible for NO_x offgasing and radical source effects in environmental chamber experiments are not currently understood, though complex wall models based on aqueous chemistry and other considerations have been developed (e.g., see Jeffries et al., 1999). For the preliminary survey in this work, we use a highly simplified wall model to account for both of these effects. In particular, both NO_x offgasing and the radical source is represented by a continuous HONO input at a zero-order, time-independent rate that is adjusted to fit the chamber data. Initial NO and/or HONO, which might be formed by dark offgasing prior to the irradiation, is also added as needed to fit the data.

The wall model also must represent O_3 wall losses that, though relatively slow in Teflon film reactors, can be non-negligible in affecting O_3 in multi-day experiments. This is determined by O_3 dark decay experiments. Since O_3 dark decay experiments have not yet been employed in the new Teflon reactors discussed in this work, the O_3 decay rates measured in other Teflon reactors under dry conditions were assumed to be applicable.

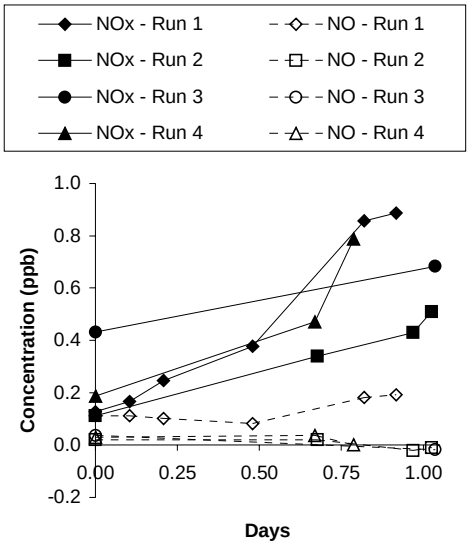
Since the "NO_x" instrument (at least in the dry runs) may be responding to nitric acid, wall loss rates assumed for HNO_3 may affect model simulations of NO_x data. For modeling these runs, relatively high HNO_3 loss rates of ~12%/hour were assumed, based on limited measurements in the SAPRC EC. The applicability of this to the Teflon reactors is highly uncertain, so modeling of the "NO_x" data should be considered to be unreliable.

C. Results and Discussion

1. NO_x Dark Offgasing Rates in the New Reactor

The results of four experiments carried out when NO_x offgasing was measured in the dark for up to one day are shown in Figure 1. It can be seen that there is no significant NO offgasing, but that there is a non-negligible buildup of "NO_x" species, with an average input rate of 0.02 ppb/hour. It does not appear to decrease significantly with time (the run numbers on the Figure caption refer to the order the runs were carried out). Note that for all these experiments the reactor was contained in an outer reactor that was continuously flushed with pure air, and sampling the air in the outer reactor indicted no detectable NO_x species. Therefore, these results cannot be attributed to permeation through the reactor walls.

Figure 1. Measurements of dark NO_x offgasing in the new Teflon reactor



Note that offgasing of either NO_2, HONO, or HNO_3 could be causing the measured "NO_x" buildup. NO_2 and HNO_3-specific analysis methods are being developed in our laboratory but are not yet available for these experiments. Model simulations of the pure air experiments, discussed below, were conducted using various alternative assumptions in this regard.

2. Pure Air and CO - Air Irradiations in the New Reactor

Figure 2 and Figure 3 show results of a pure air and two CO - air experiments carried out in the new reactor. In all three cases, significant ozone formation was observed, which could only be modeled if non-negligible NO_x offgasing is assumed. The HONO input rate used in the chamber effects model was adjusted to fit the data, and the rates that fit the O_3 data were 0.1 ppb/hour for the pure air run and 0.02 ppb/hour for the CO - air run. Note that the HONO input rate determination in the pure air run is much more uncertain than in the CO - air run. To fit the data for the pure air run, we also assumed a background VOC level equivalent to 1 ppm, though this is highly uncertain.

Figure 2. Experimental and model simulation results of a pure air irradiation in the new Teflon reactor. The data were simulated using an assumed background VOC level equivalent to 1 ppm CO, initial HONO or NO_2 of 0.8 ppb, and a constant HONO input rate of 0.1 ppb/hour.

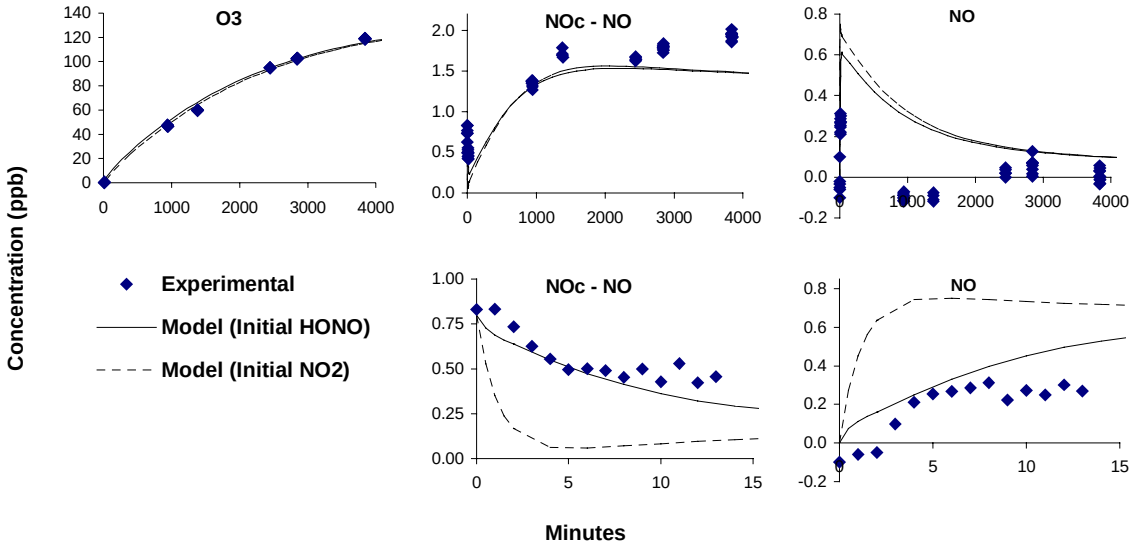
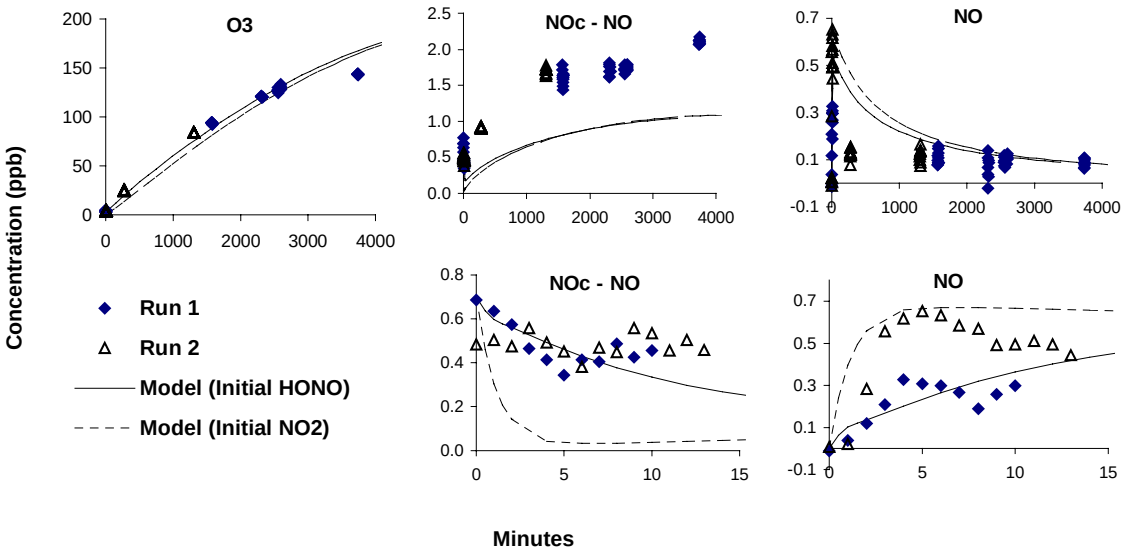


Figure 3. Experimental and model simulation results of two CO - air irradiations in the new reactor. Initial CO was approximately 25 ppm. The data were simulated using initial HONO or NO_2 of 0.7 ppb, and a constant HONO input rate of 0.02 ppb/hour.



An interesting result observed in these experiments was that the NO concentrations rapidly increased when the lights were first turned on, but then declined as O_3 formation occurred. The peak level of NO formed at the start was comparable to the initial NO_x in the CO - air run, but was about half the initial NO_x in the pure air run. The rapid formation of NO at the

start of the run means that much if not most of the initial NO_x is in the form of NO_2 or HONO, whose photolysis would result in the formation of NO. HNO_3 is relatively unreactive, and its presence would not cause the observed formation of NO.

Two model simulations are shown on each figure, one based on assuming that the initial measured NO_x is all in the form of HONO, and the other assuming it is all in the form of NO_2. Note that both models give essentially the same results except for the first ~20 minutes of the irradiation. If the NO_x is assumed to be in the form of NO_2, the NO formation occurs very rapidly, and there is a corresponding rapid decrease of NO_x-NO. The formation rate of NO and loss rate of NO_x-NO is slower if initial HONO is assumed, because the photolysis rate of HONO is slower than that of NO_2. The initial NO_x-NO data for both experiments and the NO data for the pure air run are most consistent with the assumption that all the initial NO_x is HONO, and this is also consistent with the assumption that the radical source is due to HONO offgasing. On the other hand, the maximum NO concentration in the CO - air run is better fit by the model assuming initial NO_2.

In both experiments the total NO_x levels were observed to increase during the first day of the run, and then eventually level off at ~2 ppb. The model predicts that most of the "NO_x" at the end of the experiment is in the form of NO_2, though this is based on assuming relatively rapid wall loss rates of HNO_3. The model tends to underpredict the final NO_x levels, suggesting that HNO_3 may be persisting in the gas phase longer than assumed in this model.

3. TVA Chamber Experiments

The experimental and model simulation results of the two TVA acetaldehyde - air experiments are shown on Figure 4 and Figure 5. The model simulations shown each use HONO input rates in the wall model that were adjusted so the simulation would fit the ozone data. In both cases the model simulations with the NO_x input rates adjusted to fit the ozone data tended to slightly underpredict the PAN formation, though probably not by much more than the experimental uncertainty. In the case of the 9/22/95 experiment, the model that fit the O_3 data tended to underpredict the buildup of NO_x during the run, though in the 6/11/96 run both the NO_x and O_3 were reasonably well fit by the same model. Unlike the pure air and CO - air runs with the new reactor, discussed above, there was no increase in NO at the start of the experiments. However, the irradiation in these TVA experiments probably started soon after the chamber was filled with pure air, with insufficient time for significant NO_x offgasing to occur.

Figure 6 shows the experimental and model simulation results of a TVA n-butane - NO_x experiment. Good fits to the data were obtained in the first 4 hours of the experiment when the model used a radical input rate equivalent to 0.9 ppb HONO per hour. This is significantly higher than the NO_x input rates that fit the acetaldehyde - air experiments.

Figure 4. Experimental and model simulation results of the TVA acetaldehyde - air run 9/22/95. The model simulation uses a HONO input rate of 0.09 ppb/hour.

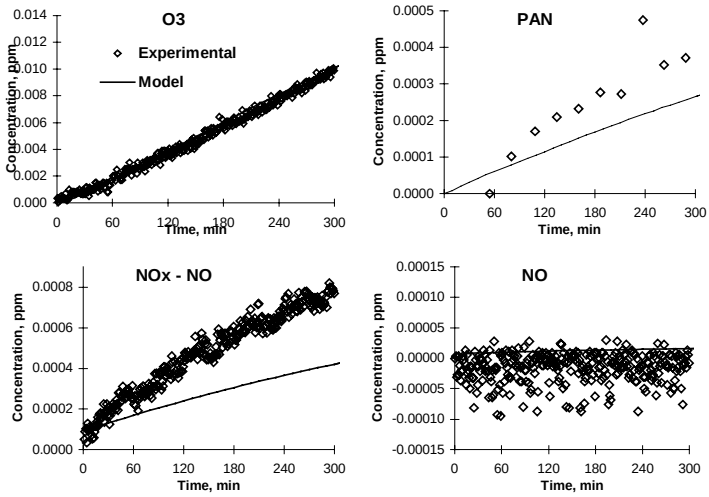


Figure 5. Experimental and model simulation results of the TVA acetaldehyde - air run 6/11/96. The model simulation used a HONO input rate of 0.16 ppb/hour.

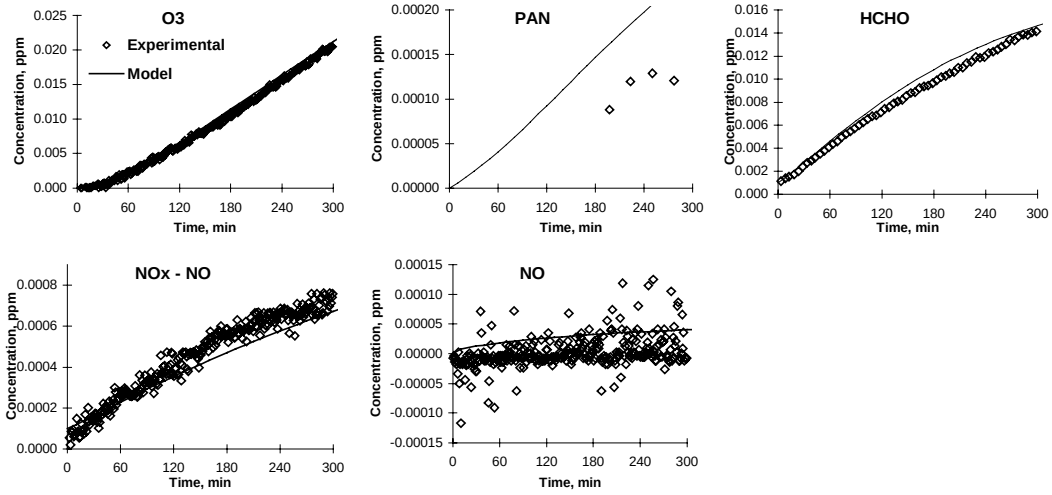
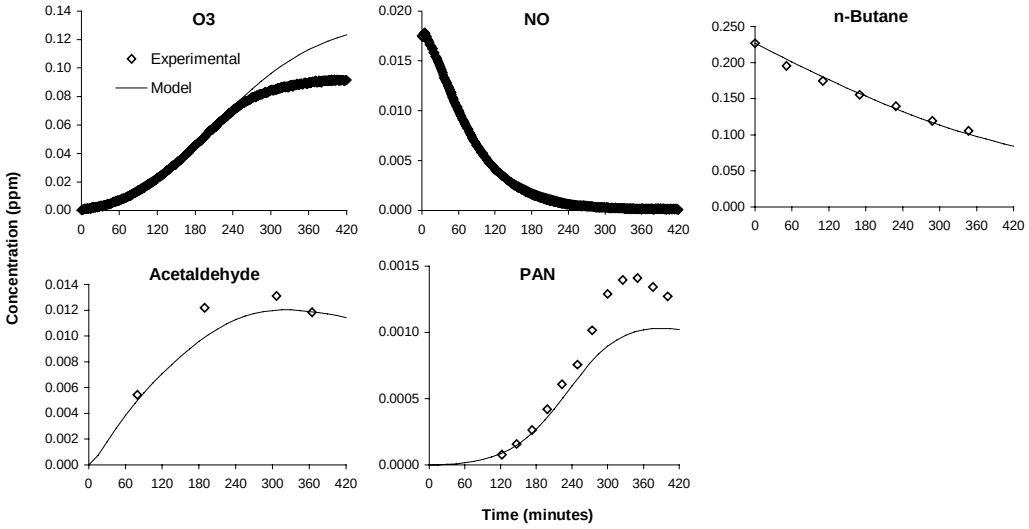


Figure 6. Experimental and model simulation results of TVA n-butane - NO_x experiment 6/19/95. The model simulation used a HONO input rate of 0.9 ppb/hour.



4. DTC Chamber Experiments

Experimental and model simulation results of the DTC acetaldehyde - air experiment that was carried out after the reactors had been extensively used for reactivity experiments are shown on Figure 7. The results in the two paired reactors were essentially the same. (NO data are not shown because the NO monitor used for this run is insufficiently sensitive to give useful NO data in such runs.) The model used a HONO input rate of 0.39 ppb/hour, adjusted to approximately fit the O_3 formation rate. The model also gave a good fit to toe observed NO_x buildup, but tended to underpredict PAN. However, the PAN analyzer used during this period did not tend to give very reliable data.

A large number of n-butane - NO_x experiments are carried out in this chamber to characterize the chamber radical source. The HONO input rates that tend to give the best fits to the NO oxidation rates in those experiments tend to vary from run to run, within the range of 0.4 to 1 ppb/hour.

5. EC Chamber Experiments

The experimental and model simulation results of the acetaldehyde - air experiment carried out in the SAPRC EC are shown on Figure 8. The model simulation that fit the O_3 data corresponded to a HONO input rate of 5.3 ppb/hour, significantly higher than observed in the all Teflon reactors, discussed above. The model also gave a good simulation of the rate of NO_x buildup observed during the run, though tended to underpredict the PAN, to about the same extent as observed in the other acetaldehyde - air experiments. Although the NO_x readings corresponded to an initial NO_x of ~12 ppb, this is probably an interference or improper zeroing of the instrument, since if 12 ppb of initial NO_2 or HONO is assumed in the model, then the model significantly overpredicts the initial O_3 formation rate.

Figure 7. Experimental and model simulation results of the acetaldehyde - air experiment DTC764. The model used a HONO input rate of 0.39 ppb/hour.

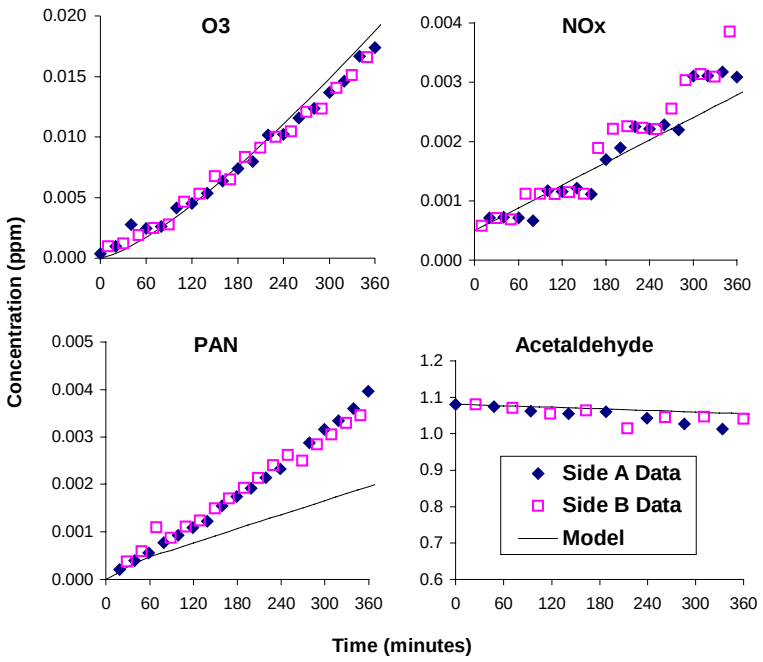
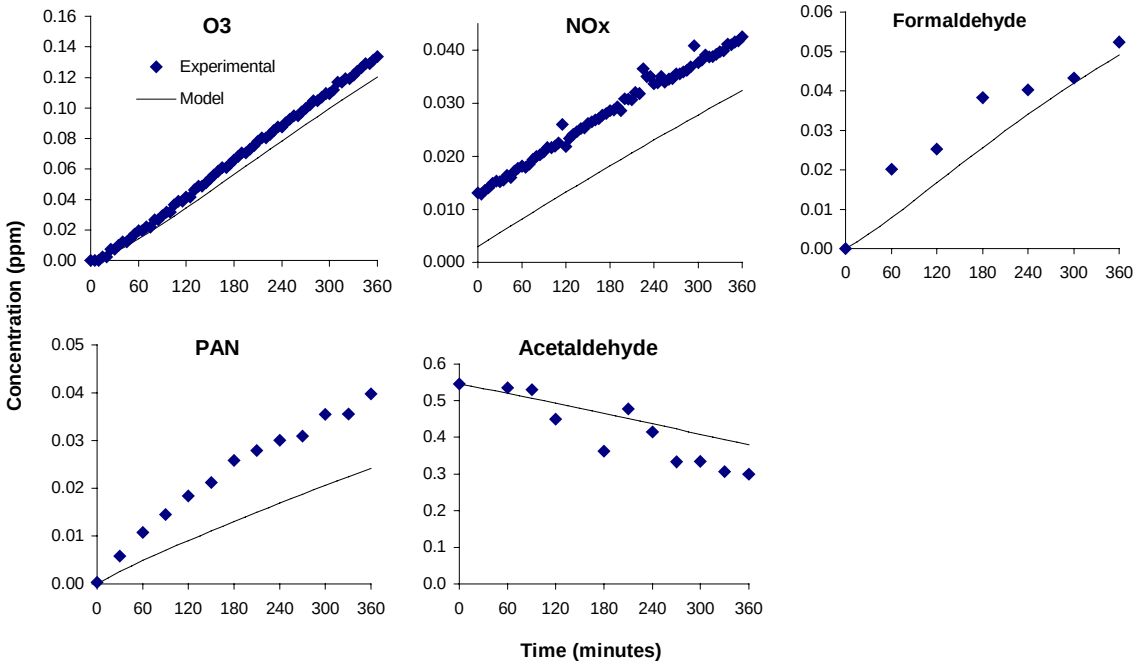


Figure 8. Experimental and model calculation results for the acetaldehyde - air experiment EC253. The model uses a HONO input rate of 5.3 ppb/hour, and an initial NO_x concentration adjusted to fit the initial O_3 data.



Analysis of NO_x-air (Carter et al, 1982) and modeling of n-butane - NO_x experiments (Carter et al, 1995a,b) indicate that the radical source in the SAPRC EC tends to be dependent on NO_x levels, and a standard wall model for the radical source in this chamber was developed based on these data (Carter et al, 1982, 1995a). For the conditions of the acetaldehyde - air experiment EC253, this wall model assumes a radical input rate corresponding to a NO_x input rate of 5.3 ppb/hour, in excellent agreement with the NO_x input rate that fit the O_3 data in the this experiment.

6. Summary of Results

Table 2 shows a summary of the results of the NO_x offgasing and radical source characterization experiments for the chambers discussed here. The NO_x offgasing rates can be seen to be the lowest in the clean, unused reactor, with the lowest NO_x offgasing rates that fit the data in the two CO - air runs being comparable to the average of the NO_x offgasing rates observed in the dark. The NO_x offgasing rates that fit the data in TVA chamber runs were somewhat higher than observed in the clean, unused reactor, but was a factor of 3-4 times lower than observed in the DTC. The NO_x offgasing rate observed in the EC was over an order of magnitude higher than that observed in the DTC or other all-Teflon chambers, indicating that the surface of that chamber is much more reactive. This is despite the fact that the between-runs cleaning in the EC is probably much more thorough than in the other chambers (with the possible exception of the TVA chambers), since the chamber is completely evacuated.

The NO_x offgasing rates observed in the TVA chamber, the DTC, and the EC can be compared with the apparent radical source input rates observed in these chambers. In the case of the DTC and EC, the radical source rates are essentially the same as the NO_x input rates, to within the variabilities and uncertainties of the determinations. This is consistent with the hypothesis that both the radical source and NO_x input are due to the same factor, presumably HONO offgasing. On the other hand, the apparent radical source in the TVA n-butane - NO_x experiment was 6-10 times higher than the NO_x input rates observed in the acetaldehyde - air runs. Either the acetaldehyde - air runs are not representative of the conditions of the n-butane experiment, or there is another radical source process involved in this chamber, or there is a problem with the particular n-butane experiment that was modeled.

D. Conclusions and Near Term Work Planned

The experiments with new, unused reactors are incomplete and still underway, and the analysis of the TVA chamber data is incomplete, so the conclusions arising from the work discussed above must be considered to be preliminary. Nevertheless, the following conclusions can be made:

- New Teflon film has non-negligible NO_x offgasing, with the minimum offgasing rate observed in this work being ~0.5 ppb/day. This is enough to cause significant ozone formation over a period of a one day irradiation. The source of this NO_x is unknown, since the reactor has not been knowingly exposed to high levels of NO_x in previous experiments. The possibility of permeation is ruled out because the reactor was inside a flushed bag with NO_x levels below 0.1 ppb.
- The apparent NO_x offgasing rates causing O_3 formation in irradiated reactors is not always higher than the rate of NO_x offgasing in the dark. Therefore, the NO_x offgasing process may not necessarily be light induced, at least for very clean Teflon reactors.

Table 2. Summary of results of modeling NO_x offgasing and radical source characterization runs in various chambers.

Run	Type	Light Intensity (k_1, min-1)	HONO Input (ppb/hr)
Clean, Unused Reactor (FEP Teflon film)			
Various	Average for Dark Experiments (NOx input)	0	0.02
9/13 - 9/17	Pure Air	0.8	0.10
9/17 - 9/21	CO - Air	0.8	0.02
9/28 - 9/30	CO - Air	0.8	0.02
TVA Chamber (Low NOx Studies) (FEP Teflon film)			
9/22/95	Acetald - Air	0.4	0.09
6/11/96	Acetald - Air	0.4	0.16
6/19/96	n-Butane - NOx	0.4	0.9
DTC (Well-used chamber) (FEP Teflon film)			
DTC764	Acetald - Air	0.2	0.4
Various	n-Butane - NOx	0.2	0.4 - 1.0
EC (Teflon coated aluminum with Quartz Windows)			
EC253	Acetald - Air	0.3	5
Various	n-Butane - NOx	0.3	5

- There is indirect evidence that most of the offgased NO_x in the new, clean reactors is mostly in the form of HONO. This is consistent with the observation, at least in some chambers, that the apparent radical source is about the same as the NO_x offgasing rates. However, the radical source rate in the new Teflon reactors have not yet been measured, and the radical source observed in at least one TVA n-butane run is much higher than the NO_x offgasing rates indicated by the data of the acetaldehyde - air runs.
- As might be expected, the NO_x offgasing rates are higher in well-used reactors than in new reactors. The multi-day light flushing procedure used with the TVA chamber appears to reduce the NO_x offgasing rate, though not to the levels observed in new, clean reactors.
- The SAPRC evacuable chamber, which has Teflon coated metal and quartz surfaces, has significantly higher NO_x offgasing and radical source rates as the all Teflon chambers. This indicates that this type of chamber is less suitable for conducting low NO_x experiments than all-Teflon reactors.

Work to better characterize the NO_x offgasing effects from new reactors is still underway, with the ultimate goal being not only to better understand these effects, but also to learn how to

design environmental chamber systems where these effects are minimized and predictable. The following near term work is planned:

- Luminol NO_2 analyzers are being developed to monitor NO_2 at the low levels needed to provide useful data to evaluate NO_x offgasing effects, and to determine the contribution of NO_2 in the NO_x offgased in the dark.
- Additional pure air and CO - air experiments are being conducted to better evaluate the reproducibility of the NO_x offgasing from new reactors. One should expect it to eventually decrease with time.
- The effects of heat, changes in light intensity, humidity, and exposure to various NO_x species on NO_x offgasing rates will be assessed.
- The effectiveness of heating, prolonged flushing in the light, various cleaning procedures, and possibly other treatments in reducing NO_x offgasing will be assessed.
- The use of other types of materials for reactor surfaces is being assessed. The data discussed above that surfaces such as in the SAPRC EC will not be satisfactory, and preliminary experiments in an all-glass chamber indicate that that type of chamber also has a higher radical source (unpublished results from this laboratory). We are having discussions with DuPont Co. about Teflon film characteristics and alternatives, and use of reactors using other types of Teflon film will be investigated.

The results of this investigation will be used to determine the design for the "next generation" chamber for generating mechanism evaluation data at very low NO_x levels. Although it is unlikely that zero NO_x offgasing can be obtainable in practice, it is important to determine the best chamber design and operating procedures to minimize these effects, and to understand and be able to predictively model what cannot be eliminated.

E. References

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